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Calcined Aceh Bovine Bone (*Bos indicus*) Intercalated Lithium as An Inorganic Base Catalyst for Transesterification of Castor Oil

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Abstract – Realizing abundant availability of local bovine bone wastes in Aceh Province, Indonesia, this study is subjected to take competitive advantages from the local bovine bone waste for preparing an inorganic catalyst preparation. In detail, calcined Aceh bovine bones were successfully intercalated lithium through an impregnation method resulting in the inorganic base catalyst, which showed promising activity in the transesterification of castor oil. Before the experiment, the Aceh bovine bone waste was calcined at 900°C in the air atmosphere for 4 hours, led to forming crystalline phases of hydroxyapatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$] and calcium oxide [CaO]. Also, the chemical modification of calcined-bovine bone with lithium precursor has enhanced the physicochemical properties of the inorganic base catalyst. Finally, the intercalated Aceh bovine bone has shown a feasible activity in the transesterification of castor oil into biodiesel, which yielding methylricinoleate as the main product.

Keywords: Aceh bovine bone, lithium, castor oil, transesterification, biodiesel

Introduction

It has been well known that the bovine meat is the highest animal protein consumed widely in Aceh, Indonesia (Dinas Peternakan dan Kesehatan Hewan Provinsi Aceh, 2011). Usually, the meat dishes served as the main menu in various events, including wedding ceremony, Ramadan, and other events which are annually held among people. Meanwhile, the processed bone is discarded into the environment as biomass wastes. Empirically, the meat consumption in Aceh continues to increase every year, resulting in high bone disposal into the environment. Regrettably, there are no scientific researches to utilize the local bovine bone waste for beneficial products to date.

The global society is currently facing a real energy problem as a direct impact due to the fossil source decreased significantly (Umbach, 2010). Realizing fossil fuels is a non-renewable energy source so that several research topics related to any renewable energy innovation have become the most attractive issues for global scientists (Syah, 2006). Among various renewable energy sources, biodiesel has been recognized as a promising candidate to replace fossil fuel in the future (Prihandana, 2006). This is due to biodiesel has several competitive advantages used to energy source, which are more inexpensive, easily synthesized from vegetable oils or animal fats through transesterification process, biodegradable and low-global warming impact, which is significantly different compared to fossil fuel (Liu, 2008). Regarding biodiesel production, transesterification is noticed as the most efficient and popular synthesis methods used to produce biodiesel using vegetable oils and animal fats as feedstocks (Syah, 2006). Nevertheless, transesterification processes require high temperature, high pressure, and a long time operation, so that the biodiesel productions become disadvantage economically (Herman, 2006). To overcome these disadvantages, a catalyst was introduced in transesterification system, so that the reaction can be realized at low pressure and temperature, mainly using a heterogeneous inorganic catalyst (Obadia, 2006).

Alkaline earth compounds are an excellent catalytic activity in the transesterification process of

triglyceride. Among those heterogeneous inorganic catalysts, the calcium oxide (CaO) based catalyst has been popularly used because it has competitive economic value, whereas its easily and naturally derived from biomass waste like animal bone and shell wastes (Hui et al., 2019). However, the alkaline earth compounds have good activity when it's supported on specific materials, e.g., alumina compared to its unsupported catalyst. On the other side, the basicity and catalytic activity of CaO can also be enhanced through the promotion of alkali metals on their surfaces (Watkin et al., 2004). The impregnation CaO using Li, Na, K on CaO can improve the physicochemical properties and catalyst activity of CaO.

In contrast, the CaO doped Li shows better activity on the transesterification of Karanja oil compared to CaO catalyst doped with Na and K (Meher et al., 2006; Jinshan et al., 2018; Liu, 2008; Keene, 2004). Concerning economic and green material to use for inorganic catalyst preparation, bovine bone waste has become an alternative biomass waste to utilize for derivating alkaline earth metal oxides, primarily CaO based catalysts. Practically, highly thermal treatment on these bones waste under the air atmosphere could be resulting in inorganic metal oxides based on alkaline and alkaline earth metal oxides (Neyda, 2008). However, to enhance the catalytic performance of alkaline and alkaline earth metal oxides, which are existed in the calcined bovine bone catalyst, the obtained catalyst popularly modified with other metal elements, whether through chemical or physical methods.

To our best scientific consideration, lithium doped inorganic catalyst has performed high activity in various organic synthesis (Diez, 2006; Leveles, 2003; Almquist, 2000). In the detailed investigation, the Li-doped MgO catalyst showed promising activity in the transesterification of vegetable oil for biodiesel compounds (Zhenzhong, 2010; Macleod, 2008). Unfortunately, there is no report on the modification of calcined bovine bone with lithium, so that scientific investigation, especially in the intercalation of calcined bovine bone with lithium, is needed to be realized. This study was proposed to derivate heterogeneous catalysts based on CaO from Aceh's local bovine bones waste through a physical method, which is then chemically modified with Li-promoter through an impregnation method. To understand its catalytic performance, the obtained catalyst is applied for the transesterification reaction of castor oil into biodiesel.

Materials and Methods

Materials

Materials used in this study are Aceh local bovine waste, castor oil, aquadest, and filter papers. While the equipment consisted of a set of reflux equipment, measuring flasks, thermometers, and electronic heaters equipped with a stirring control and temperature control.

Lithium Intercalation on Calcined Bovine Bone

Bovine bone materials obtained from a local meat market in Banda Aceh, Aceh Province. These bones were washed using deionized water and then were boiled at 100 °C for four hours to remove any impurities attached to the bone surface. The cleaned bones were then dried for 24 h at 100 °C in a laboratory heater and then grinded into a fine powder and sieved toward bone powder with a particle size of 150 µm. The bone powder was then calcined at 900 °C for 4. These Physicochemical properties of these calcined products were characterized using X-ray diffraction (XRD) with Cu target metals at a voltage of 40.0 kV and a current of 30.0 mA (Rigaku Smart Lab SE). Meanwhile, the surface morphology and percentage of elements in the material were analyzed using Scanning Electron Microscope-Energy Dispersive Spectroscopy (FEI Inspect –S50). Several amounts of the calcined kept for the intercalation process using a lithium precursor.

The intercalation process was started by transferring the calcined powder of local One was separated into glass vessels. An incipient impregnation was used to intercalate lithium on the calcined local bovine bone pore using lithium nitrates precursors of 3wt % and recalcined at 550°C for 5 hours. To obtain its physicochemical properties, the synthesized catalysts were analyzed using X-Ray Diffraction, SEM-ED Sand Bruenauer-Emmett-Teller (BET) Method simultaneously.

Transesterification Reaction of Castor Oil

Refined castor oil was collected from local markets in Medan, North Sumatra Indonesia. To remove any solid impurities and water molecules, the vegetable oil was filtered and heated at 110 °C for 30 minutes. The transesterification process refers to the previous procedure, as reported by Padil *et al.*, (2010), with a few modifications, as explained in the following illustration. The reaction process was carried out in a 100 ml three necks round bottom flask equipped with a reflux condenser and agitated stirrer. At an early

stage, the esterification was done. The raw castor oil has poured into the three-neck flask, and the addition of methanol at oil - methanol molar ratio was 12: 1.

Furthermore, 0.8 ml of Sulfuric acid was added to the solution, and the esterification process was carried out at 65 °C for 60 minutes. The esterification product cooled at ambient temperature and then transferred into a separated funnel for the separation process within 24 hours. The upper liquid, which assumed as triglycerides product, was taken out for used as feedstock for transesterification reaction.

The transesterification process was done as follows: some amount of lithium intercalated calcined bovine bones (5wt %) was introduced into methanol under the stirring process. The castor oil obtained from the esterification process added into the mixture and heated at 60 C for two hours under the stirring process at a fixed speed of 600 rpm. The transesterification product was transferred into a separated funnel and left for 24 h for completely divided into three-phase after 24 h at room temperature. The upper layer of the liquid phase was taken out as crude biodiesel, while the lower layer was glycerol mixed with remaining methanol. The upper layer assumed as methyl ester was transferred into another sample container for physicochemical and GC analysis to have qualitative information of the contained biodiesel.

Results

Intercalating Lithium on Calcined Bovine Bone

Calcination process has caused decomposition of compounds existed in bone material so that the bone color changed from light brown to white, as shown in Fig 1. Intercalation is a simple method used to introduce a substance (metal, oxide) on the surface of a porous solid material. The process aims to change the physicochemical properties of a material, so that it has competitive advantages, as it's expected. Figure 1 showed the dried bovine bone particle (a) and (b) calcined bovine bone particles. As can be seen, the calcined process changed bone, and lithium intercalated bone catalyst was characteristic as white color particles.

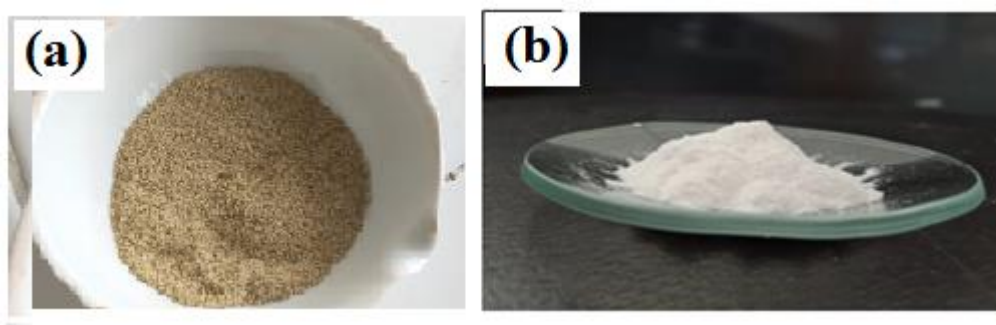


Figure 1. (a) Dried bovine bone particles; and (b) Calcined bovine bone particles (900 C, air atmosphere)

To understand how the thermal treatment and intercalation process impacted to the crystalline phase of local bovine bone, a XRD analysis was used in this experiment. The crystalline phase was analyzed based on matching results between each peak of the obtained XRD diffractogram with the joint database Committee on Powder Diffraction Standards (JCPDS). Specifically, the XRD pattern obtained in the experiment had been matched with the JCPDS database by detecting the angles of 2θ and both crystal gap.

Figure 2 represented the obtained XRD pattern of calcined bovine bone particles (a), and Calcined bovine bone catalyst intercalated lithium (b). It can be assumed that the calcination process changed CaCO_3 to CaO (JCPDS-96-900-6747), and $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, as it referred to JCPDS numbers of 96-900-4537. Impregnation of lithium on calcined bovine bone particles enhanced the crystallization phase of CaO and $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ as well.

Figure 3 (a) showed SEM micrographs both calcined bovine bone and lithium intercalated bovine bone catalyst. It can be seen that calcined bone particles have an irregular shape with their size that tends to the nanoscale. Lithium addition on the calcined bovine bone surface was not changed the morphological structure of calcined bone particles used, as can be seen in Fig. 3 (b).

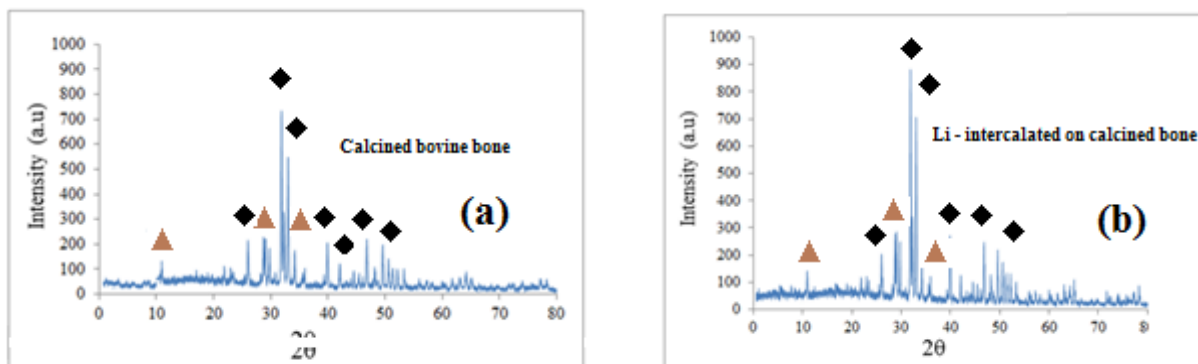


Figure 2. XRD Diffractogram of (a) Calcined bovine bone; (b) Lithium intercalated bovine bone catalyst (Li- the content of 3 wt.%).

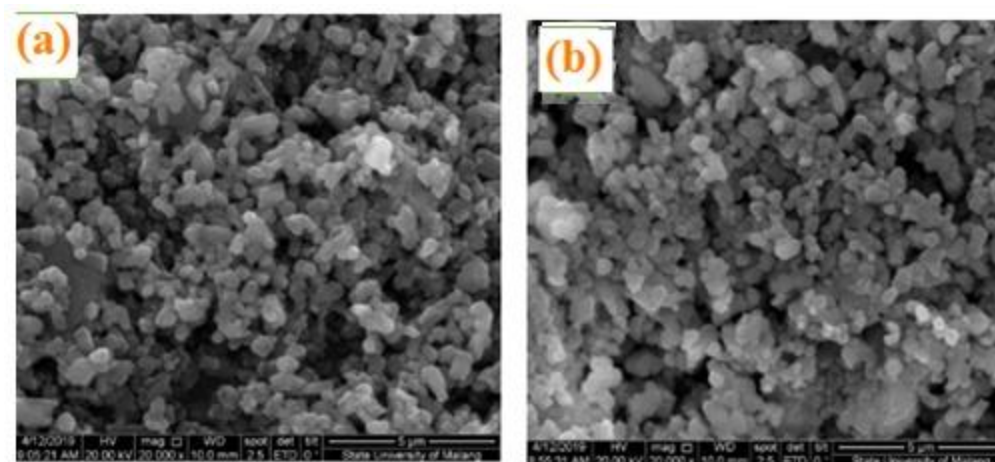


Figure 3. SEM micrographs of (a) Calcined bovine bone; (b) Lithium intercalated bovine bone catalyst (Li- the content of 3 wt.%).

Table 1. The result of the BET analysis of calcined bovine bone and Lithium intercalated bovine bone catalyst (Li- the content of 3 wt.%)

Number	Sample	Surface area (mg ² /g)
1.	Calcinedbovinebone	11.127
2.	intercalatedbovinebone catalyst (Li- the content of 3 wt.%)	4.358

Table 1 showed the total surface area of calcined bovine bone and Lithium intercalated bovine bone catalyst, which determined through the BET method. As the represented data are shown in table 1 above, it can be assumed that the lithium particles have been successfully intercalated on the bone surface both inner and outer pore sides resulting in decreasing of bone surface area from 11.127 m² / g become 4.358 m² / g.

Catalytic Study for Transesterification of Castor oil

Figure 4 showed the biodiesel product that resulted in the transesterification process using a lithium intercalated bovine bone catalyst, which prepared in this experiment. The transesterification was conducted by employing castor oil and methanol with the experimental condition as follows: molar ratio of castor oil to methanol was 1:12, time reaction of 2 h and catalyst weight of 5 wt.%.



Figure 4. Obtained biodiesel from castor oil transesterification catalyzed by lithium intercalated bovine bone catalyst (Li- 3 wt%)

Table 2 represented four main methyl ester compounds obtained in The experiment. Therewasmethyl linoleate (11.78%), methyl oleate (7.78%), methyl stearate (3. 38), and methyl ricinoleate (77.29%), as the primary substances in the biodiesel product.

Table 2.The composition of the obtained biodiesel

Compound	Peak Area (%)
Methyl Linoleate	11.78
Methyl Oleate	7.78
Methyl Stearate	3.14
Methyl Ricinoleate	77.29

Discussion

Calcination is the process of stable material decomposition due to heat energy transfer. This process takes place at high-temperature conditions, e.g., 900 °C in oxygen or air environment. Based on the results of the matching process of the obtained XRD pattern with database JCPDS, as shown in Fig. 2, it appeared some specific intensity at 2θ of 31.9 and 32.1, which represented hydroxyapatite compound $[\text{Ca}_{10}(\text{PO}_4)_6 (\text{OH})_2]$ after the calcination process on the bovine bone sample. This is reasonable because the fresh bovine bones contained calcium carbonate (CaCO_3) as the main compounds composed of the bone material. However, while a calcination process (900 °C) carried out to the bovine bone particles, it changed this calcium carbonate (CaCO_3) into calcium oxide (CaO) by releasing CO_2 into the air, as it has reported by Ooi, C. Y, et. Al (2007). The continuous heating process caused a reaction between CaO particles with phosphate ions in the bones resulting in a hydroxylapatite compound, which indicated by its characteristic peak at its specific value of 2θ, as it represented through the XRD pattern in Figure 2 above. However, the CaO particles still appeared at the final step of the calcination process, which meant the calcination process on the bovine bone at 900 could not change CaO into hydroxylapatite particles completely. On the other hand, the intercalation of lithium on the calcined bovine bone surface has led positive impact in which increasing the crystallization process of the hydroxylapatite particles, as it seems in Figure 2b above. There are no lithium crystal peaks detected. This can be understood due to the small degree of li crystals formed on calciningbone sample so that it could not be adequately seen as a limit sensitivity of the XRD equipment used.

To find out the effect of the calcination treatment and lithium impregnation on the bovine bone structure, a physical analysis using SEM has been carried out. Figure 3 showed the SEM micrographs obtained in this study. The figure shows that calcination of bovine bones produces irregularly shaped particles of small size, forming small assemblages between particles. Based on these SEM micrographs, Ir

can be state that there was no significant impact on the particle shape and size after lithium impregnated on the calcined bone sample.

Table 1 showed the total surface area samples, both calcined bovine bone and calcined bone, impregnated lithium samples determined using the BET method. As can be seen, the entire surface area of calcined bone decreased around 60%. This phenomenon indicated that the impregnation process had introduced the lithium nitrate phase into the crystal lattice of hydroxyapatite and CaO, which contained the bovine bone samples. Further calcination process has caused lithium species attached on the surface and near the surface of the CaO and hydroxyapatite crystals in the bone samples resulting in a positive impact on CaO and hydroxyapatite as heterogeneous catalysts for the biodiesel synthesis.

Catalytic Study in Transesterification of *Castor oil*

The content of fatty acid methyl ester (FAME) found in crude biodiesel products can be useful for determining a catalyst activity which used in a transesterification process. The content of fatty acid methyl ester (FAME) compounds in a crude biodiesel product can be useful for determining the activity of a catalyst used in a transesterification process. Figure 4 shows the crude biodiesel produced in this study. The analysis using GC demonstrated the composition of the crude biodiesel consisted of methyl linoleate (11.78%), methyl oleate (7.78%), methyl stearate (3.38), and methyl ricinoleate (77.29%), as the main substances in the biodiesel product. The results of this study provide scientific evidence regarding a prospective performance of the lithium intercalated bovine bone catalyst for the transesterification of castor oil at low temperature and pressure conditions.

Conclusion

Lithium intercalated bovine bone catalyst has been successfully prepared in this study and applied as an inorganic base catalyst for biodiesel synthesis from castor oil. Lithium impregnation on calcined bovine bone has been enhancing the crystalline growth of hydroxyapatite and CaO in the bovine bone matrix. Lithium intercalated bovine bone catalyst showed feasible activity for transesterification of castor oil into biodiesel resulting in methyl ricinoleate the primary product.

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